Final Preparation Guide

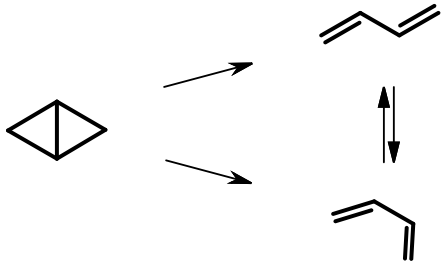
(Chem 111, Fall 2013)

The final will test your knowledge and understanding of all the topics and techniques that we have covered in this class. Your three recommended study sources are the textbook(s), the posted tutorials, and the notes that you took in the class. Some of the posted tutorials were used as my lecture notes and I expect that you know all the background material presented there. Others demonstrated how to solve kinetics problems with *Mathematica*; you do not need to know the mathematical details of these solutions by heart. Below is a list of important topics that we have covered since the second midterm. Please consult Midterm Guides for other important topics that you should know.

1) Transition state theory
    a. The potential energy surface and the reaction path
    b. Mathematical properties of minima and saddle points
    c. Basic assumptions and principles of transition state theory
    d. The properties of the molecular partition function
    e. The Eyring equation
    f. Quantum mechanical determination of transition state structures
    g. Quantum mechanical determination of activation free energies
    h. Kinetic isotope effect and tunneling

The Final has two parts. The first in-class part is similar to the in-class part of your midterm exams. The main differences are that questions are more integrative, and your answers are worth a lot more on the final than they were on the midterms. Also, the final may have a larger fraction of multiple-choice and true-false type questions. The second, take-home part has the following questions:

1) Unimolecular isomerization of bicyclo[1.1.0]butane to 1,3-butadiene is an electrocyclic reaction that can occur ether via conrotatory or disrotatory pathway. The reaction product, 1,3-butadiene, exist as a rapidly interconverting mixture of *s*-cis (this is most likely slightly bent, and thus more correctly called *s*-gauche) and *s*-trans isomers at temperatures where this reaction can be observed.



    a) Use Kinetics Database of NIST Chemistry Webbook to obtain the rate constant of this reaction at 200 °C. (2 pts)

b) Use your organic chemistry textbook and explain terms "conrotatory pathway" and "disrotatory pathway" in the context of this reaction. (4 pts)

c) Read the paper titled "*A comparative assessment of the perturbative and renormalized coupled cluster theories with a noniterative treatment of triple excitations for thermochemical kinetics, including a study of basis set and core correlation effects*" (and, optionally, related papers by Prof. Piotr Piechuch), and discuss the advantages of the CR-CC(2,3) method in calculation of activation barriers in electrocyclic reactions such as isomerization of bicyclo[1.1.0]butane. (4 pts)

d) Calculate the rate constant for the unimolecular process that consists of internal rotation around the carbon–carbon single bond in 1,3-butadiene (at room temperature) using the HF/aug-cc-pVTZ quantum mechanical method. Compare your result with one published value from the literature; provide the reference you used. Outline the process you took to obtain the rate constant, and show the key calculations. (10 points)

Extra credit. Calculate one of the transition states for the unimolecular isomerization of bicyclo[1.1.0]butane to 1,3-butadiene using one of the quantum mechanical methods that takes into account the electron correlation. Compare your calculated activation energy with the experimental value. As part of the answer, include the image of the transition state that shows the distance between C1 and C4. (10 pts)